Preface

Alumina silica and aluminosilicate minerals are widely distributed in nature They are used as high temperature materials and have many speciality applications such as catalyst supports and low thermal expansion co-efficient materials In addition to widespread use in the field of pigments and photo-catalysts titania and titanates are also versatile electro-ceramics Fumed alumina silica and titania owing to their nanosize offer a plethora of speciality applications The use of non-oxide ceramics such as Si_3N_4 and SiAlON is directed towards replacement of metal components in gas turbine and internal combustion engines Aluminium nitride belongs to a short list of non-metallic solids with a high thermal conductivity which offers exciting prospects in electroceramic industry for packaging microelectronic components

The present investigation is aimed at Flame synthesis of fumed alumina silica titania and their composites Investigations on the reactivity of fumed oxides in the preparation of mullite, tialite nitrides oxynitrides and SiAlON are of interest Sintering and microstructure of these materials continue to attract the attention of Materials Scientists and Engineers

The thesis comprises of Five Chapters First chapter is devoted to the literature survey on fumed oxides nitrides and oxynitrides The synthetic methods used properties and applications of these materials are discussed in detail The scope and objectives of the present study are highlighted

Second chapter describes the principles of Instrumental and Analytical techniques used in the present study Instrumental techniques used are X - ray powder diffraction Infrared spectrophotometry electron microscopy (SEM/EDXS TEM) ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy BET surface area measurement by continuous flow method, particle size analysis by Laser Scattering and Differential thermal analysis Analytical techniques used include gravimetric analysis of SiO_2 Al_2O_3 TiO_2 and ZrO_2 nitrogen estimation in refractory nitrides and determination of surface silanols Synthesis of diformyl hydrazide (DFH), methylaluminium sesquichloride (MASC) aluminium bromide etc have also been described Purification methods used for nitrogen and liquid ammonia are highlighted

Chapters 3 and 4 contain the results of present investigations. Chapter 3 describes the preparation, properties and reactivity of fumed alumina, silica, titania and their composites by flame hydrolysis of respective metal halides. Three flames, H_2-air, CH_4-air and LPG-air have been used. Large surface area (82-115 m^2/g) nanosize (~20 nm) fumed alumina has been prepared by the flame hydrolysis of $AlCl_3$, $AlBr_3$ and MASC. Similarly, fumed silica and titania having surface areas 210 m^2/g and 64 m^2/g have been obtained by the flame hydrolysis of $SiCl_4$ and $TiCl_4$ respectively using H_2-air flame.

Fumed silica is always amorphous while fumed alumina and fumed titania show crystallinity in the as-formed state. The infrared spectra show absorptions in the region of 3800-3500 cm^{-1} due to the presence of surface hydroxyl groups. Fine particle, large surface area (45-80 m^2/g) mullite ($3Al_2O_3 \cdot 2SiO_2$) and tialite (Al_2TiO_5) precursors could also be prepared by the flame hydrolysis of $AlBr_3$-$SiCl_4$/$TiCl_4$. Mullite and tialite phases evolve from these reactive precursors below 1000°C. The crystallization and sintering behaviour of the fumed oxides can be modified by the addition of KNO_3, ZrO_2, Al_2O_3, SiO_2 etc. Mullite and tialite could be sintered to 98% theoretical density by the addition of ZrO_2 and SiO_2 at 1600°C and 1350°C respectively. Microstructure of the sintered bodies show controlled grain growth. An appendix to Chapter 3 contains the results of rheological studies on fumed silica.

Fourth chapter is devoted to the investigations on Nitrides (Si_3N_4 and AlN) and Oxynitrides (Si_2N_2O and SiAlON). Technologically important Silicon nitride (Si_3N_4) has been prepared by the direct ammonolysis and carbothermal reduction and nitridation of fumed silica as well as imide ($Si(NH)_2$) pyrolysis. Silicon nitride obtained by the imide process is X-ray amorphous having large surface area (≈170 m^2/g) and high reactivity. On calcination at 1450°C in N_2 atmosphere, amorphous Si_3N_4 is converted to α-Si_3N_4 which when sintered at 1650-1750°C, 3h in the presence of MgO, Y_2O_3, Al_2O_3, achieves 96% theoretical density. β-SiAlON has been prepared by the combustion of heterogeneous solution containing α-Si_3N_4, $Al(NO_3)_3$-Urea/DFH as well as solid state reaction between fumed alumina and amorphous Si_3N_4.

The product is characterized by XRD. Fine particle β SiAlON having 40-50 m^2/g surface area when sintered at 1650°C 3h after incorporation of Y_2O_3 achieved 97-98% theoretical density. Single phase aluminium nitride (AlN) has also been prepared by carbothermal reduction and nitridation of fumed alumina.

Last chapter summarises the results and conclusions of the present investigation.